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Next 1 Page(s) In Document Denied

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THERMOOXIDATIVE DEGRADATION OF POLYPHENYLPOLYDIMETHYLSILOXANES

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Polyorganosiloxanes have received widespread attention as heat resistant materials. They have great significance in (the) industrial electrolytic materials, in some films, for high temperature usage.

Thermooxidative destruction of many typical polyorganosiloxanes has been studied in (this) line of work as applied to pure polymers in the powder state, in the form of films on a copper or aluminum substrate and in connection with the glassy fabrics of saturated polymers.

This work was a study of the thermooxidative resistance of certain polyorganosiloxanes. Among the criteria of this thermooxidative resistance were changes in weight (loss) and changes in adhesive ability of the polymeric fibres.

The thermooxidative resistance was defined at 300°, 350°, 375°, 400° and 500° C. and continued in operation at the high temperatures for 90 days at 300° C. and 96 at 500° C. (The) loss of weight was defined on a specimen of pure polymer in the form of a film measuring 50 x 100 mm., 0.05 mm. thick. The polymer film was on aluminum foil 0.01 mm thickwith subsequent solution of the aluminum substrate by HCl. The film was heated in a soecial steel box with double walls, built of heat-insulating material.

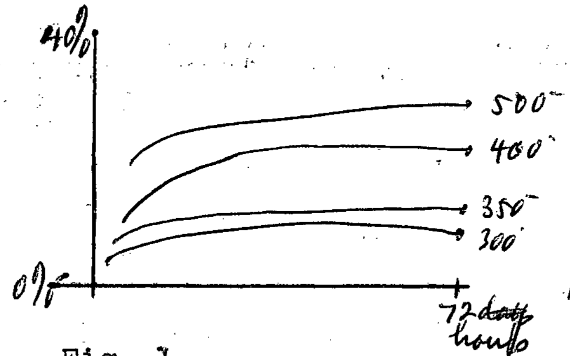

Fig. 1
Change in Weight Loss of Polymer 1 During Aging
300°-500° C

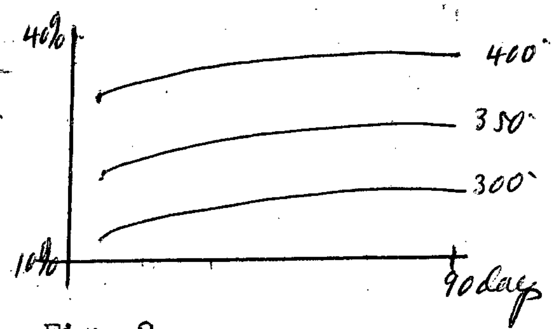

Fig. 2
Same for Polymer 1
300°-400° C

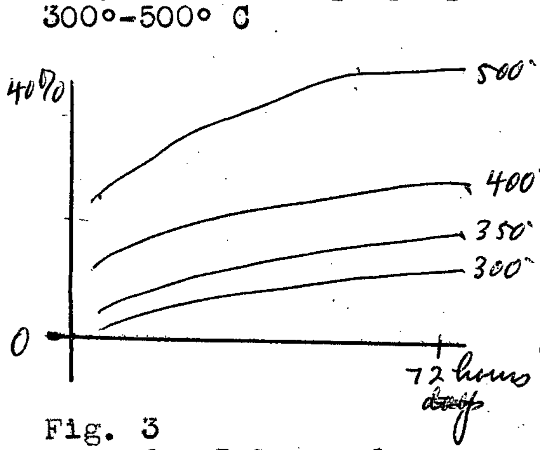

Fig. 3
Same for Polymer 2
300°-500° C

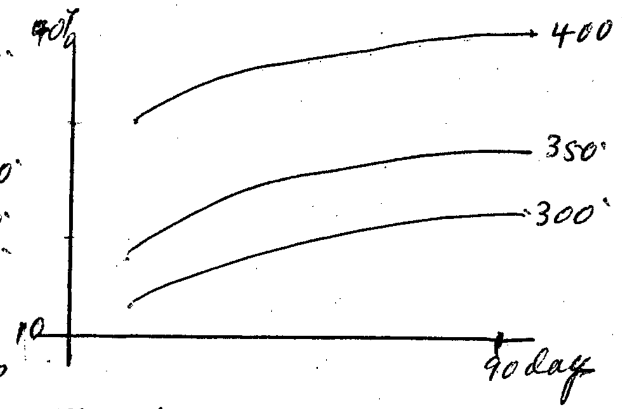

Fig. 4
Same for Polymer 2
300°-400° C

In figures 1-4 experimental data (are shown) on the loss of weight of polymers 1 and 2 in dependance on time at 300°-500° C.

From the shape of the curves it is evident that the loss of weight of the pure polymers has fundamental significance (indicating) a character-change between 300° and 350° C- the curves are close (in these areas) and the higher temperatures of 400°-500° C. accentuate the loss of weight, especially of polymer 2.

Polymeric film No. 1 remains without noticeable change even after 720 hours at 300° C., 168 hours at 350° C, and 24 hours at 400° C. Further warming brought to light a crack in the film after it had been cooled to 20° C.In the polymeric film No. 2 a crack appeared after heating 2160 hours at 300° C., 336 hours at 350° C. and 48 hours at 400° C.

The second criterion of change in the properties of polymers 1 and 2 under operating temperatures was afforded by the change in adhesive ability of these polymers as films. This criterion was based on six segments of copper wire with a glassy insulator (PSDKT), impregnated with solutions of polymers 1 and 2 and pressed at 250° C., a measured load (in kg.) necessary for rupture in the middle of the wire. This loading determined the strength of the attachment (to the) wire of the polymeric film.

In figures 5-8 are shown experimental curves of the changes in properties of polymers 1 and 2 during the process of warming up to 300° - 500° C. From these runs in the curves it was seen that adhesive ability decreases with heat and time.

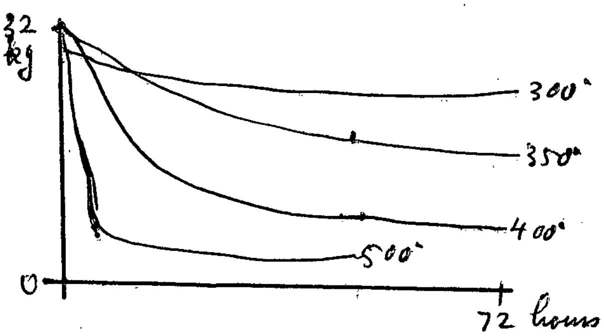

Fig. 5
Change in Adhesive Ability of Polymer 1, During Aging between 300° C and 500° C

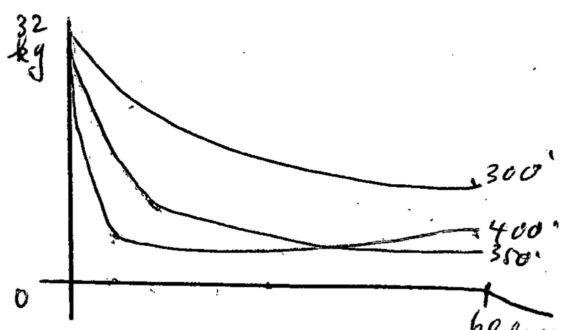

Fig. 6
Same, between 300°-400° C.

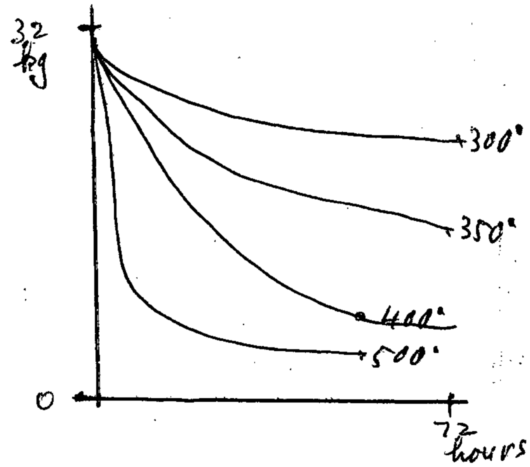

Fig. 7
Same, Polymer 2 between
300° and 500° C.

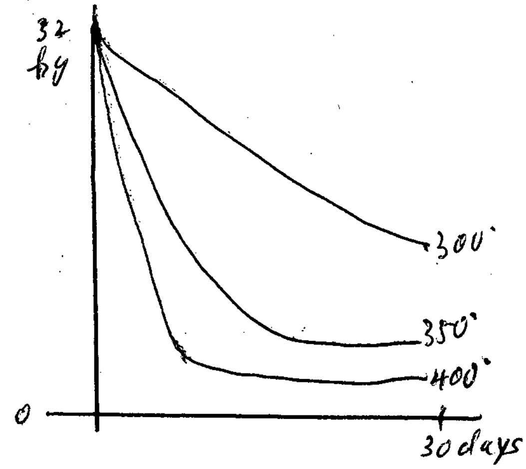

Fig. 8
Same, Polymer 2
between 300° and 400° C.

Thus from these data, with the help of (acceptable) methods a (picture) could be set up of the factors involved and the relationship of loss of weight and adhesive ability of the polymers 1 and 2 to time at different temperatures.

The curves in figures 9 and 10 show loss of weight and change in adhesive ability of polymers 1 and 2 during the heating process, corresponding to points (determined) earlier. The presence of large numbers of points on the curve diminishes the probability of error in the process of carrying out the experiment and allows the gathering in addition, of information which turns out well (and of value) in the explanation of experimental results.

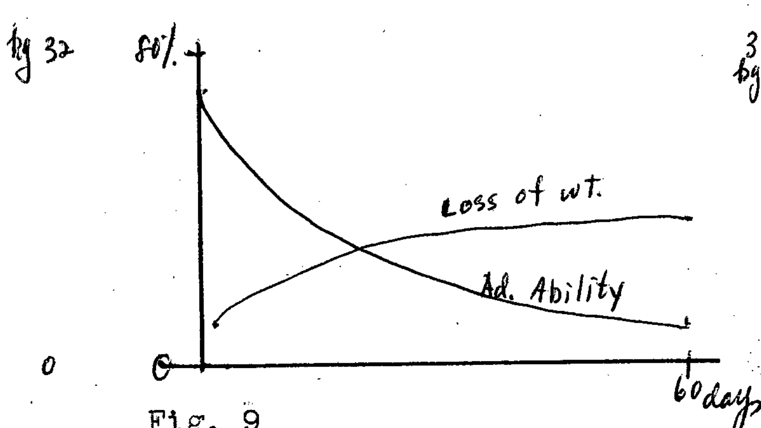

Fig. 9
Change in Adhesive Ability and
Weight Loss, Polymer 1 (300°-500° C)

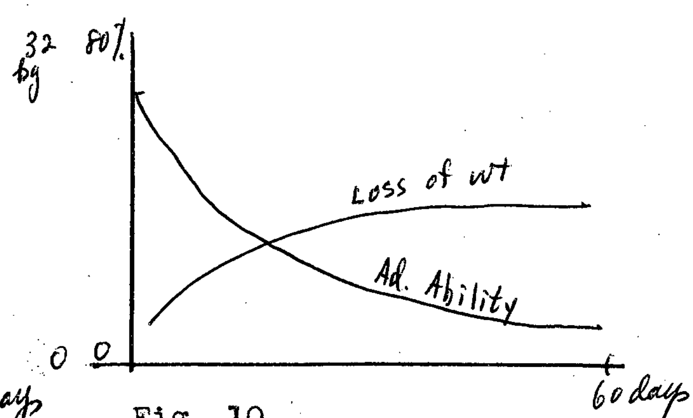

Fig. 10
Same, Polymer 2

On the abscicca there is time of aging in hours at the temperature of 500° C., in days at an aging temperature of 400° C, weekly at 350° C. and monthly at 300° C. On the ordinate are magnitude of loss of weight (in %) and adhesive ability (in kg.).

In the run shown in the curves it is obvious that the points, in accordance with the amount of weight loss at 300°, 350°, 400° and 500° C. for different times of aging are very close, the scattering is slight. The points belonging to the curve showing change off adhesive ability are quite meaningful however. Regular change in adhesive ability of the polymers was adhered to at all temperatures with a continuation of weight-cycle(?) aging.

As seen in figures 9 and 10, for each polymer (there is) definit e significance in the loss of weight definitely tied in with adhesive ability. From this (relationship) parameter there was constructed a curve of the effective life of the polymer on the generally-accepted logarithmic scale.

As will be seen in figures 11 and 12, there is (herein) shown the logarithmic curve of the life of the polymers 1 and 2 in the temperature interval of 300°-500° C., with the points indicating loss of weight always lying on a straight line.

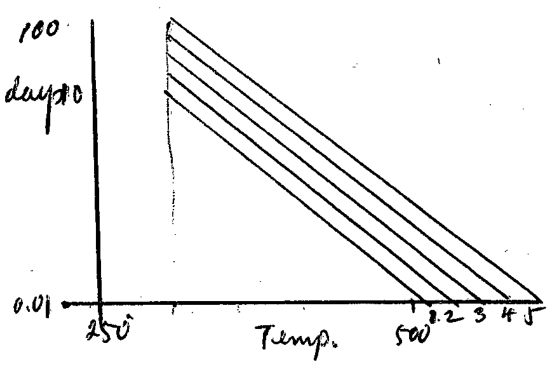

Fig. 11
Effective Life, Logarithmic, Polymer 1

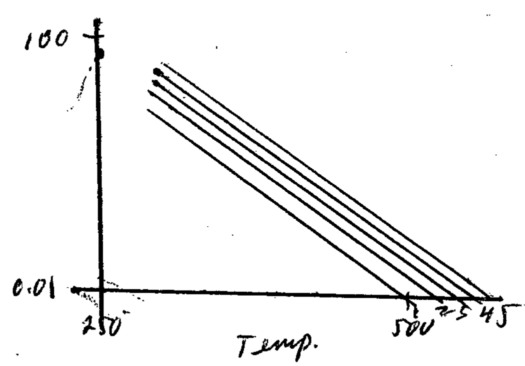

Fig. 12
Same, Polymer 2

Fig. 11:
Loss of weight % 1-18, 2-21, 3-32, 4-27, 5-30.
Adhesive Ability kg, 1-15, 2-11, 3-9, 4-5, 5-4.

Fig. 12
Loss of weight % 1-18, 2-21, 3-22, 4-27, 5-30.
Adhesive Ability 1-9, 2-7, 3-6, 4-4,5, 5-4.

Comparing figures 11 and 12, we see that though of comparable significance with respect to loss of weight, they have different significance (with regard to) adhesive ability. Here, the time of effective life of polymer 2 lengthens. For example, correlated with an 18% loss of weight, adhesive ability of polymer 1 is 15 kgs., of polymer 2 2-9 kgs, and the length of life at 350° C. accordingly runs to 84 and 168 hours. However, when aging occurring in stages, in connection with loss of weight, reaches 30% the difference in size or magnitude of adhesive ability and the timing of polymers 1 and 2 diminishes considerably, then disappears entirely. So, the effective life time curvesof both polymers beginning at 30% loss of weight coincide with that for the amount of adhesive ability, 4 kgs.

It is assumed that the velocity of aging, that is, measurement of the relationships in this study of polymers in the process of aging, follows the Arrhenius equation:

$$a_t = A\, e^{\frac{-E}{RT}}$$

where a_t is speed of aging, A is a probability constant, E the energy of activation in kcal per mole, R the gas constant and T the absolute temperature.Them, knowing the data from the literature (2) or from earlier experiments for the value of the energy of activation, it is easy to determine the effective life of the polymer at any temperature.

In the table on the effective life of polymer 1, determinations were made from experimental data and from calculations by means of the energy of activation, 32 kcal per mole.

MEASUREMENT OF EFFECTIVE LIFE OF POLYMER 1 IN RELATION TO AGING TEMPERATURE

Aging Temperature °C.	Effective Life Experimental	Effective Life Calculated
300	1440	1428
350	168	168
375	72	68
400	24	24
500	1	1

As (will be) seen from this table, (the) experimental data are close to the calculated.

SUMMARY

1. A study of the resistance to thermooxidation by films of certain polyorganosiloxanes at temperatures between 300° C. and 500° C.

2. The evidence (shows) great thermooxidative stability on the part of the polymeric films studied.

LITERATURE

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2. N.N.Sokolov, Methods of Synthesis of Polyorganosiloxanes, ibid (1959)
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